



Catalytic oxidation of ammonia: A pre-occupied-anchoring-site strategy for enlarging Ag nanoparticles at low Ag loading and achieving enhanced activity and selectivity on Ag-CuO_x/Al₂O₃ catalyst

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ABSTRACT

The Ag nanoparticles (AgNPs) in Ag/Al₂O₃ catalysts play a crucial role in the selective catalytic oxidation of NH₃ (NH₃-SCO). To enhance NH₃-SCO activity, Cu, which has stronger anchoring ability than Ag, is introduced onto Al₂O₃, reducing available anchoring sites for Ag. As Ag cannot displace anchored Cu species, Ag species agglomerate into larger AgNPs even with low Ag loading. Consequently, these enlarged AgNPs become more active centers for NH₃-SCO. The optimal Ag:Cu molar ratio is confirmed as 2:3. This 'pre-occupied-anchoring-site' strategy decreases Ag loading to 1/5 of the original, reducing catalyst costs while maintaining activity. *In situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) studies reveal that NH₃-SCO on 2Ag1.8Cu/Al (weight ratio) catalyst follows the hydrazine mechanism below 200 °C, coexisting with the imide mechanism from 200–250 °C, and solely the imide mechanism beyond 250 °C. This strategy is applicable to various transition metals, including Mn, Co, Ni, and Fe, promoting cost-effective AgNPs formation.

1. Introduction

Ammonia (NH₃) has been confirmed to play a crucial role in the formation of haze pollution, and gaseous NH₃ can damage the human respiratory tract and plant leaf stomata [1,2]. NH₃ in the atmosphere mainly comes from the spontaneous production in nature and human activities. Anthropogenic sources mainly include animal husbandry, agriculture, industry and transportation [3–5]. Moreover, with the increasingly stringent NO_x emission standards implemented around the world, under the large-scale application of deNO_x technologies such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), the aggravation of NH₃ slip problems is inevitable [6,7].

Therefore, the development of efficient and inexpensive NH₃ purification technology is receiving increasing attention in both academia and industry.

At present, selective catalytic oxidation of NH₃ (NH₃-SCO) to N₂ and H₂O is the most effective NH₃ purification technology. Catalysts with precious metals as active components such as Pt, Pd, Rh, Au, Ir display high NH₃-SCO performance [8–17]. Although most transition metal-based catalysts (such as Cu, Fe, Co and Mn *etc.*) also have certain NH₃-SCO catalytic activity, they are not suitable for NH₃ removal from stationary sources and indoor air due to their inferior performance at low temperatures [18–24]. Ag-based catalysts have been widely studied in NH₃-SCO due to their broad operation temperature window and

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relatively low cost [25–28]. Our previous studies showed that Ag nanoparticles (Ag_{NPs}) are the intrinsic active centers for NH_3 -SCO reaction [29]. The H_2 reduction pretreatment and increasing the Ag loading (usually up to 10 wt%) are common methods to improve the NH_3 -SCO performance of Ag-based catalysts [29–31]. However, on one hand, the high-temperature reduction pretreatment using H_2 has potential safety hazards and also increases the energy consumption. Meanwhile, the Ag_{NPs} formed by agglomerating the Ag species in H_2 at high temperatures are easily redispersed in oxygen-rich atmosphere, making it difficult to maintain high catalytic stability [32]. On the other hand, increasing Ag loading to improve the NH_3 -SCO activity will increase the catalyst production cost considerably. In addition, the N_2 selectivity in NH_3 -SCO on pure Ag-based catalysts is usually low, which is an obvious drawback that needs improvement. To resolve these issues, Ag–Cu dual site catalysts have been developed with remarkable success in the NH_3 -SCO reaction [26,33], with higher catalytic activity and N_2 selectivity than single-component catalysts. However, the performance of these catalysts remains suboptimal, necessitating operation under reaction conditions characterized by a gas hourly space velocity (GHSV) below $30,000 \text{ h}^{-1}$ and a reaction temperature exceeding 270°C to achieve 100% NH_3 conversion. Furthermore, the catalytic stability of these high-loading Ag–Cu catalysts remains untested for practical applications.

In our previous work, it has been reported that the terminal hydroxyl groups on $\gamma\text{-Al}_2\text{O}_3$ are the anchoring sites for Ag atoms [34]. Therefore, the abundant terminal hydroxyl groups on Al_2O_3 support are favorable for the dispersion of Ag as single atoms, while the Ag species tend to agglomerate to form Ag clusters and Ag_{NPs} when the terminal hydroxyl groups are insufficient for Ag anchoring. The abundant Ag_{NPs} in Ag-based catalysts are beneficial to the substantial improvement of catalytic performance in NH_3 -SCO reaction. However, obtaining high-concentration Ag_{NPs} on Al_2O_3 often requires more Ag loaded, which leads to an increase in the catalyst cost. In this study, we propose a 'pre-occupied-anchoring-site' strategy using Cu, an inexpensive transition metal with higher anchoring strength to Al_2O_3 , to occupy the anchoring sites on Al_2O_3 surface in advance. Thus, Ag can be forced to agglomerate into Ag_{NPs} due to the lack of anchoring sites, and the conversion rate of NH_3 can be greatly improved. Meanwhile, as an effective promoter, Cu addition can significantly improve the N_2 selectivity as well, and finally improve the overall catalytic performance in the NH_3 -SCO reaction. Additionally, the 'pre-occupied-anchoring-site' strategy proves to be universal, as observed with Co, Fe, Mn, and Ni, forcing Ag species to agglomerate into Ag_{NPs} and consequently enhancing NH_3 -SCO performance.

2. Materials and methods

2.1. Catalyst preparation

The catalysts were prepared using the wet impregnation method. Initially, 5 g of $\gamma\text{-Al}_2\text{O}_3$ was mixed with deionized water to create a suspension under stirring. Subsequently, an aqueous solution containing 0.1 g of Ag and varying amounts of X metal (where X represents Cu, Co, Mn, Fe, and Ni) was added to the suspension in the form of an aqueous nitrate solution. After 3 h of impregnation, the mixture was dried using a vacuum rotary evaporator. Further, the samples were dried at 105°C for 12 h and calcined in air at 550°C for 3 h. Finally, the catalysts were sieved to 40–60 mesh and given specific names, such as 2AgxX/Al , where 2 indicates 2 wt% loading of Ag, x denotes the loading of X metal, and Al denotes Al_2O_3 . If no Ag or X was added, the samples were referred to as xX/Al or 2Ag/Al . For example, in the 2Ag1.5Cu/Al and 2Ag1.6Co/Al samples, the Ag loading was 2 wt% and the molar ratio of Ag:Cu and Ag:Co was 2:3. The 2Ag/Al and 1.2 Cu/Al reference catalysts were also prepared and both had the same metal loading in moles as $9.26 \times 10^{-4} \text{ mol/5 g support}$. The catalysts, which were subjected to pretreatment with 10 vol% H_2/N_2 for 2 h at different temperatures, were named

2Ag-T/Al and 1.2Cu-T/Al , where T represents the pretreatment temperature.

Based on the aforementioned preparation, an appropriate quantity of synthesized 2Ag/Al or xCu/Al was mixed with deionized water, forming a suspension. Next, an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ or AgNO_3 was added to achieve a loading of x wt% Cu or 2 wt% Ag, respectively. Following the impregnation for 3 h, the mixture was dried using a vacuum rotary evaporator. Subsequently, the samples were dried at 105°C for 12 h and calcined in air at 550°C for 3 h. The resulting samples were named xCu/2Ag/Al or 2Ag/xCu/Al , respectively.

2.2. Sample characterization

A Thermo Nicolet iS-50 equipped with an MCT/A detector was used to perform *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to measure the change in anchoring sites for Ag or Cu species and to study the NH_3 -SCO reaction mechanism. The sample was pretreated before measurement with 20 vol% O_2/N_2 at 500°C for 30 min. In typical experiments, 500 ppm NH_3 or a mixture of 500 ppm NH_3 + 10 vol% O_2 at a total flow rate of $300 \text{ mL}\cdot\text{min}^{-1}$ was introduced into the DRIFTS cell. All spectra were recorded at $800\text{--}4000 \text{ cm}^{-1}$ by accumulating 100 scans with a resolution of 4 cm^{-1} .

In situ Fourier transform infrared spectroscopy (FTIR) experiments in the transmission mode were also conducted on a Thermo Nicolet iS-50 with a high-vacuum chamber (base pressure of $< 5 \times 10^{-8} \text{ mbar}$).

Powder X-ray diffraction (XRD) measurements were performed on a computerized PANalytical Empyrean diffractometer with a $\text{Cu K}\alpha$ radiation source.

Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS) for elemental mapping were conducted on an FEI talosf200s. The Ag dispersion was calculated based on the average Ag particle size from the STEM images.

Diffuse reflectance ultraviolet–visible (UV–vis) spectra were measured at room temperature in the air using BaSO_4 as a reference (U-3100 UV–vis spectrophotometer, Hitachi Co., Japan). All UV–vis spectra were collected at 190–800 nm with a resolution of 1 nm.

In situ Raman spectra were obtained using a Renishaw Via Raman Spectrometer equipped with an *in situ* reaction chamber. The excitation source was an air-cooled 633-nm laser with an output power of 150 mW.

Ag K-edge X-ray absorption fine structure (XAFS) spectra, including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), were recorded in the fluorescence mode at room temperature using Beamline 7-BM QAS of the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. Cu K-edge XAFS spectra, including XANES and EXAFS, were collected in fluorescence mode at the BL14W beamline of the Shanghai Synchrotron Radiation Facility. Data were analyzed using Athena and Artemis from the Demeter software package. The filtered k^2 weighted $\chi(k)$ was Fourier-transformed into R-space with a k range of $2\text{--}12 \text{ \AA}^{-1}$.

H_2 temperature-programmed reduction (H_2 -TPR) experiments were performed using a Micromeritics AutoChem II 2920 apparatus. All samples were pretreated at 500°C for 30 min under 20 vol% O_2/Ar and then cooled to 50°C , followed by Ar purging for 20 min. Further, the H_2 -TPR profiles were obtained by passing a flow of 10 vol% H_2/Ar through the sample from 50°C to 800°C (with a ramping rate of $5^\circ\text{C}/\text{min}$). H_2 consumption was continuously monitored using a thermal conductivity detector.

2.3. Density functional theory (DFT) calculations

The anchoring strength of Ag and Cu atoms on the hydroxylated $\gamma\text{-Al}_2\text{O}_3$ surface was calculated using the density functional theory (DFT) method in the formalism of the Perdew–Burke–Ernzerhof (PBE) functional [35] with the van der Waals correction proposed by Stefan Grimme (i.e., DFT-D3 method) [36], as implemented in the Vienna ab

initio simulation package (VASP 5.4.4) [37]. The projector augmented wave (PAW) method was used to describe the core-valence electron interaction [38], and a cutoff energy of 400 eV was adopted during the calculations. Based on our previous research [39], a (2 × 2) supercell of the hydroxylated γ -Al₂O₃ (100) surface was modeled. The top two layers and the adsorbents were fully relaxed, while the bottom layers were fixed to mimic the bulk region. To avoid the periodic image interaction normal to the surface, a vacuum gap of 20 Å was applied. Structures were optimized with a conjugate gradient algorithm until the forces on all relaxed atoms were less than 0.02 eV/Å, and the 1 × 1 × 1 k-point grid was adopted based on the Monkhorst-Pack method [40]. The adsorption energies of Ag/Cu on the γ -Al₂O₃ surface were calculated as follows: $E_{ad} = E_{adsorbate+surface} - (E_{surface} + E_{atom})$, where $E_{adsorbate+surface}$, E_{atom} , and $E_{surface}$ are the total energies of the system that adsorbed Ag/Cu, single active metal atom, and the Al₂O₃ slab, respectively. E_{ad} denotes the stability of the adsorbates on the γ -Al₂O₃ surface. Negative E_{ad} values indicate that the adsorbed state is energetically favorable.

2.4. Catalytic activity test

A fixed-bed quartz tube reactor (i.d. 4 mm) was used to test the NH₃-SCO activity of the catalysts (30 mg for each testing), with the total gas flow controlled at 100 mL·min⁻¹ and the gas hourly space velocity (GHSV) as 120,000 h⁻¹. The gas composition at the reactor inlet was NH₃ (500 ppm), O₂ (10 vol%), and balance N₂. The concentrations of effluent NH₃ and NO_x were continuously monitored using an online FTIR spectrometer equipped with a 2-m gas cell and a DTGS detector. The turnover frequency (TOF) is defined as the number of NH₃

molecules converted per surface Ag atom per second. Only NO, NO₂, N₂O, and NH₃ were detected during the reaction. Therefore, the NH₃ conversion (X_{NH_3}), N₂ selectivity (S_{N_2}), and N₂O selectivity (S_{N_2O}) were calculated according to Eqs. (1) and (3):

$$X_{NH_3} = \left(1 - \frac{[NH_3]_{out}}{[NH_3]_{in}}\right) \times 100\% \quad (1)$$

$$S_{N_2} = \left(1 - \frac{2[N_2O]_{out} + [NO]_{out} + [NO_2]_{out}}{[NH_3]_{in} - [NH_3]_{out}}\right) \times 100\% \quad (2)$$

$$S_{N_2O} = \frac{2[N_2O]_{out}}{[NH_3]_{in} - [NH_3]_{out}} \times 100\% \quad (3)$$

The TOF measurements were performed in separate experiments, where the NH₃ conversion was maintained below 30% by varying the GHSV, and the TOFs were calculated according to Eq. (4):

$$TOF = \frac{\eta_{NH_3} \times Q \times (60V_m)}{(m \times w_{Ag} \times D_{Ag})/M_{Ag}} \quad (4)$$

where η_{NH_3} is the NH₃ conversion rate (< 30%), Q is the gas flow rate (L/min), V_m is equal to 22.4 L/mol, m is the mass of catalyst (g), w_{Ag} is the Ag loading (wt%), D_{Ag} is the dispersion of Ag on γ -Al₂O₃ (%) (calculated based on the average Ag particle size from STEM images), and M_{Ag} is the relative molecular weight of Ag (g/mol; the relationship between Ag size (d) and dispersion (D) is $d \text{ (nm)} = 1.31/D$) [41].

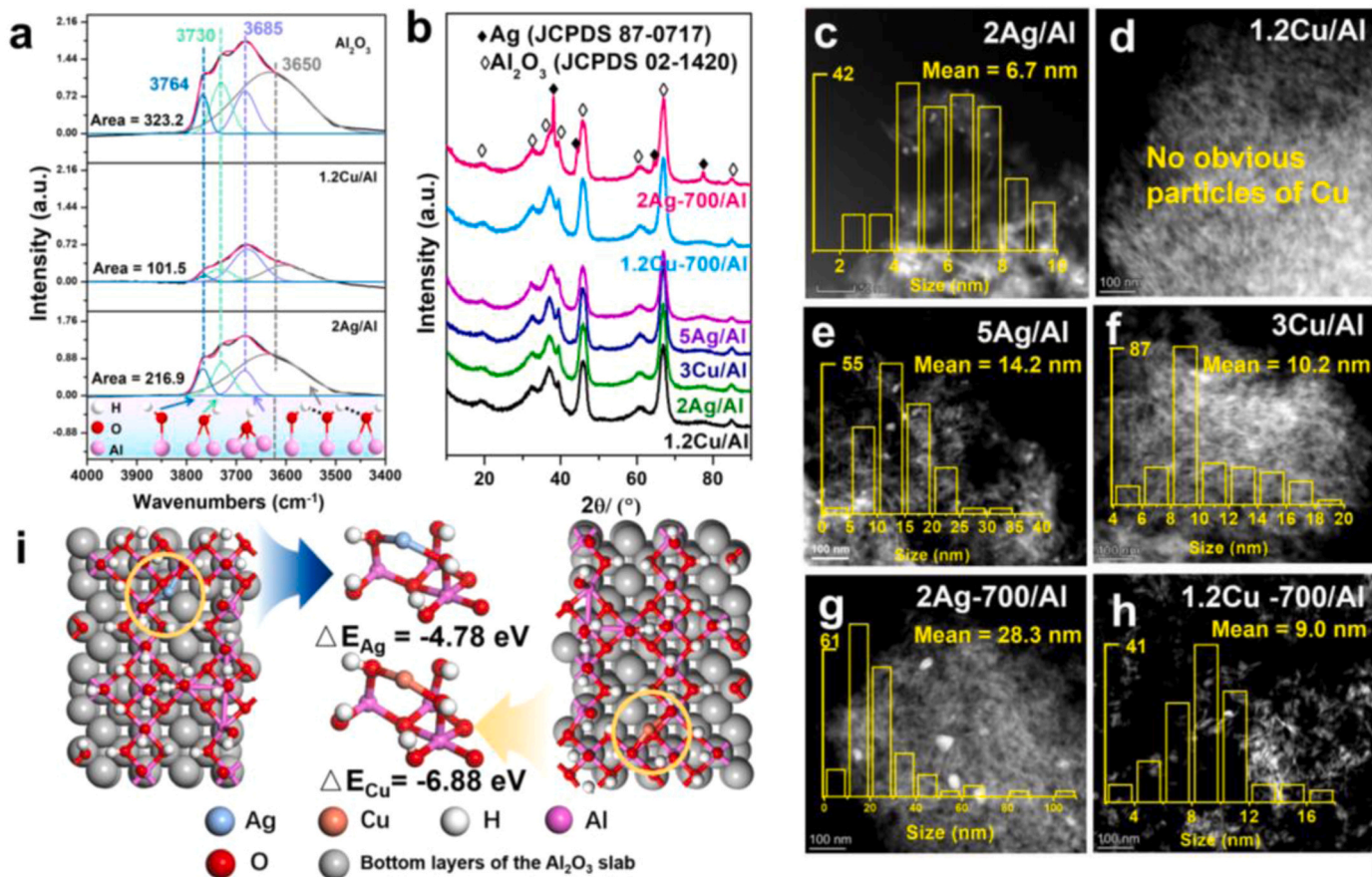


Fig. 1. The hydroxyl content of γ -Al₂O₃ support loaded with Cu or Ag; a comparison of dispersion degree of Ag and Cu species on γ -Al₂O₃; and DFT calculation of anchoring capability of Cu and Ag on γ -Al₂O₃: (a) The hydroxyl content of γ -Al₂O₃, 2Ag/Al and 1.2Cu/Al samples based on FTIR measurement in vacuum.; (b) XRD patterns; HAADF-STEM images of (c) 2Ag/Al, (d) 1.2Cu/Al, (e) 5Ag/Al, (f) 3Cu/Al, (g) 2Ag-700/Al, (h) 1.2Cu-700/Al; and (i) DFT calculation results of anchoring capability of Ag or Cu onto γ -Al₂O₃ (100) surface.

3. Results and discussion

3.1. Anchoring strength of Ag and Cu on Al_2O_3

Our previous studies demonstrated that Ag atoms anchor to the $\gamma\text{-Al}_2\text{O}_3$ surface by coordinating with terminal and doubly bridging hydroxyl groups [34]. The hydroxyl content on the $\gamma\text{-Al}_2\text{O}_3$ surface was measured by *in situ* FTIR in a high-vacuum chamber under pressure of $< 5 \times 10^{-8}$ mbar. All tested samples underwent pretreatment at 230 °C for 1 h to remove H_2O . Based on the results shown in Fig. 1a, the peaks at 3764, 3730, and 3685 cm^{-1} on Al_2O_3 , 2Ag/Al, and 1.2Cu/Al samples, respectively, could be attributed to terminal hydroxyls, doubly bridging hydroxyls, and triply bridging hydroxyls. A large and broad peak detected at 3650 cm^{-1} could be due to the presence of associated hydroxyl groups [42]. Compared with terminal and doubly bridging hydroxyls, triply bridging and associated hydroxyl groups usually exhibit lower net charges [42]. This phenomenon indicates that only the terminal and bridging hydroxyl groups are available as active anchoring sites for supported metals [43]. As expected, the terminal hydroxyls (3764 cm^{-1}) and doubly bridging hydroxyls (3730 cm^{-1}) on $\gamma\text{-Al}_2\text{O}_3$ were heavily consumed after loading both Ag and Cu [44–53]. To verify if the surface hydroxyl groups on Al_2O_3 could be reduced after calcination at 550 °C, a new set of experiments was designed, in which Al_2O_3 was added into deionized water to form a suspension and then stirred for 2 h, followed by vacuum rotary evaporation, drying and calcination at 550 °C. These treatments barely affected the hydroxyl concentration on Al_2O_3 support (Supplementary Fig. S1a). However, the hydroxyl groups on the surface of the 0.6Cu/Al, 1.8Cu/Al, 3Cu/Al, and 5Cu/Al samples clearly decreased with Cu loading (Supplementary Fig. S1b). Therefore, it can be preliminarily deduced that Cu could also be anchored through the terminal hydroxyl groups and bridging hydroxyl groups on the surface of $\gamma\text{-Al}_2\text{O}_3$ similar to Ag. When the same atomic numbers of Ag and Cu were loaded on Al_2O_3 , the detected hydroxyl peaks on the surface of Al_2O_3 were integrated as 216.9 a.u. (2Ag/Al) and 101.5 a.u. (1.2Cu/Al), respectively. Hence, the utilization efficiency of hydroxyl groups by Cu atoms should be considerably higher than that by Ag atoms.

To compare the anchoring strength of Ag and Cu on Al_2O_3 , the degree of agglomeration of the Ag and Cu species under the same loading or H_2 pretreatment condition was investigated. As shown in Fig. 1b, the 2Ag/Al, 5Ag/Al, 1.2Cu/Al, and 3Cu/Al samples did not show obvious XRD diffraction peaks of the Ag or Cu species. This suggests that the Ag and Cu species could be highly dispersed on the $\gamma\text{-Al}_2\text{O}_3$ surface without forming large nanoparticles under low-metal-loading conditions (Supplementary Fig. S2). The average particle sizes of the 2Ag/Al, 5Ag/Al, and 3Cu/Al samples were 6.7, 14.2, and 10.2 nm, respectively. Moreover, no obvious nanoparticles could be observed on the 1.2Cu/Al sample, as the STEM images shown in Fig. 1c–f. Even when the Cu loading increased to 1.8 wt%, Cu atoms remained as isolated atoms and/or clusters on the Al_2O_3 surface without forming significant nanoparticles (Supplementary Fig. S2). This result indicates that Cu species had higher dispersion degree on Al_2O_3 than Ag species. In addition, a clear difference in the agglomeration degree was observed in the 2Ag/Al and 1.2Cu/Al samples after H_2 pretreatment. The 2Ag-700/Al sample showed strong XRD diffraction peaks ascribed to the Ag crystal phase (Fig. 1b), and the average particle size of Ag was 28.3 nm (Fig. 1g). However, as shown in Fig. 1b, no significant Cu diffraction peaks were observed on the 1.2Cu-700/Al sample, and the STEM image also showed that the average particle size of Cu was only 9.0 nm (Fig. 1h), much smaller than that of Ag particles (Fig. 1g). Because H_2 reduction could break the Metal–O bond to induce the formation of metal nanoparticles, the higher Ag agglomeration degree could indirectly reflect that the anchoring strength of Ag on Al_2O_3 was much weaker than that of Cu in this study [29,32].

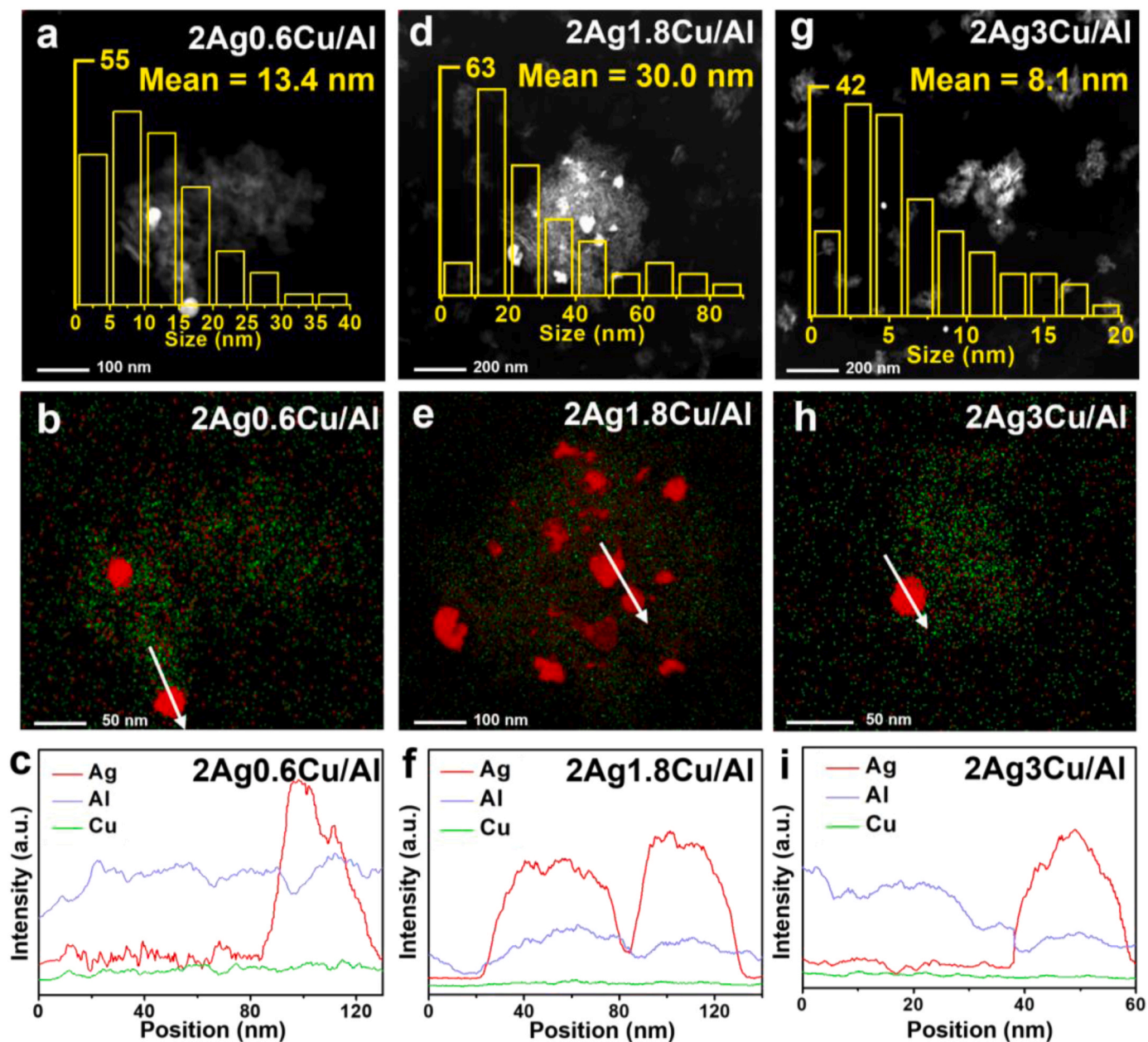
DFT calculations were performed to confirm this hypothesis and investigate the interaction between Ag and Cu species and hydroxyl

groups. Our previous study demonstrated that the terminal hydroxyl groups on the (100) surface of Al_2O_3 were the anchoring sites of Ag [34]. Accordingly, we calculated the interaction between Ag and Cu atoms and terminal hydroxyls on the (100) surface of $\gamma\text{-Al}_2\text{O}_3$. The relaxed structures of Ag or Cu binding on the hydroxylated (100) surfaces of $\gamma\text{-Al}_2\text{O}_3$ are presented in Fig. 1i. The Ag and Cu atoms can be stably bonded to the terminal hydroxyl sites, demonstrating that the (100) surface of $\gamma\text{-Al}_2\text{O}_3$ could anchor these atoms. Stable bridge-like structures with double terminal hydroxyl groups were formed on the (100) surface of $\gamma\text{-Al}_2\text{O}_3$ (Fig. 1i; orange circles), and the adsorption energies of Ag and Cu in the models were calculated as -4.78 and -6.88 eV, respectively. This result shows that Cu atoms could be more stably anchored to the (100) surfaces of $\gamma\text{-Al}_2\text{O}_3$ than Ag atoms.

The experimental results and DFT calculations demonstrated that Cu atoms could exhibit higher hydroxyl utilization efficiency and stronger anchoring strength onto the $\gamma\text{-Al}_2\text{O}_3$ surface compared to Ag atoms. These results suggest the high probability that Cu atoms preferentially preoccupy the terminal hydroxyl groups and cause the Ag atoms to agglomerate when the hydroxyl groups are insufficient on the $\gamma\text{-Al}_2\text{O}_3$ surface.

3.2. Effect of Cu loading on Ag particle size

The microstructure and compositional distribution of the nanocrystals were further investigated by STEM and EDS mapping to explore the effect of Cu loading on the Ag particle size in Ag– $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalysts. As shown in Fig. 2a–c, the Cu introduction considerably increased the size of the metal particles compared with the catalyst with only Ag. The EDS mapping results further confirmed that the composition of the observed metal particles was dominated by Ag (Fig. 2b, e, h). In contrast, Cu was mainly highly dispersed on the support surface. The sizes of Ag particles in 2Ag0.6Cu/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al were 13.4, 30.0, and 8.1 nm, respectively, which were larger than that in the 2Ag/ Al_2O_3 sample (6.7 nm; Fig. 1c). These results indicate that the Cu introduction obviously promoted Ag agglomeration. Notably, there was an optimal Cu loading to promote Ag agglomeration on the Al_2O_3 surface. The Ag particle size first increased and then decreased with increasing Cu loading, and the maximum value was reached when the Ag:Cu molar ratio was 2:3 (i.e., 2Ag1.8Cu/Al). This was due to the insufficient occupation of hydroxyl groups at low Cu loadings and the Ag redispersion on CuO particles at high Cu loadings. When the Cu loading was low, the anchoring sites were not fully occupied, and Ag could still be anchored and dispersed to a certain extent. Further, the Ag_{NPs} observed in the 2Ag0.6/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al samples all exhibited the characteristic lattice parameters of Ag (111) (Supplementary Fig. S3). The EDS line scanning results (Fig. 2c, f, i) reveal that the Cu element intensity was similar to or lower than that of the Al element. Moreover, the content of Cu species did not change considerably during the entire scanning interval. The Cu species did not show a higher signal, even in the region with a high Ag concentration. Therefore, the highly dispersed Cu species could not form an ordered CuO_x interface to anchor Ag. When the Cu loading was low, the anchoring sites were not fully occupied, and Ag could still be anchored and dispersed to a certain extent on Al_2O_3 . However, when the Cu loading reached the optimal level and continued to increase, the Cu species formed large CuO particles (Supplementary Fig. S4) and forced Ag to diffuse from Al_2O_3 to the CuO surface and redisperse (Supplementary Fig. S5). The DFT calculation results (Supplementary Fig. S6 for the adsorption energy of Ag on the CuO surface, which was $E_{\text{Ag}} = -1.87$ eV) showed that the CuO surface was indeed favorable for dispersing Ag. Therefore, the CuO particles generated under high Cu loading could act as additional anchoring sites for Ag to promote the redispersion of Ag species.



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Fig. 2. HAADF-STEM, EDS mapping, and line scanning images of 2AgxCu/Al samples: a, b, c 2Ag0.6Cu/Al; d, e, f 2Ag1.8Cu/Al; and g, h, i 2Ag3Cu/Al. Red: Ag; Green: Cu.

3.3. Effect of Cu loading on the charge state of Ag

The UV-vis spectra of the catalysts with 2 wt% Ag and different Cu loadings on Al_2O_3 are presented in Fig. 3a. The peak at 235 nm was attributed to Ag^+ ions [54]. The peak at 280 nm was assigned to the UV absorption of Ag_n^+ clusters, and the peaks at 338 and 430 nm were assigned to the surface plasmon absorption of Ag_n^0 clusters and AgNPs , respectively [55,56]. Cu species were mainly observed at 245, 299, 352, and 624 nm [26,57,58]. Therefore, among all the samples measured, only 2Ag1.8Cu/Al showed a characteristic peak of Ag^0 at 338 nm, indicating that AgNPs possibly existed in the 2Ag1.8Cu/Al catalyst. This phenomenon can also be confirmed by the XRD results (Fig. 3b). Typical diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ were present for all samples, while no Ag-containing phases were observed except for the 2Ag1.8Cu/Al

catalyst. In case of the 2Ag1.8Cu/Al catalyst, obvious diffraction peaks at 2θ of 38.1° , 44.3° , 64.5° , and 77.4° were observed, corresponding to the (111), (200), (220), and (311) lattice planes of Ag. This indicates that the Ag species within this catalyst were in a high aggregation state when the Ag:Cu ratio was 2:3. However, when the Cu loading was lower or higher than this ratio, no significant diffraction peaks of Ag^0 species were observed. This is because the low Cu loading was insufficient to make Ag fully agglomerate, and the excessively high Cu loading could lead to the formation of CuO (Supplementary Fig. S7) to disperse Ag.

Further, XAFS measurements were conducted to study the valence state and coordination condition of Ag species on 2AgxCu/Al samples with different Ag:Cu ratios (2Ag0.6Cu/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al), using Ag foil, Ag_2O , and AgNO_3 as references. The normalized Ag-K XANES (Fig. 3c) shows that the white line intensities of all 2AgxCu/Al

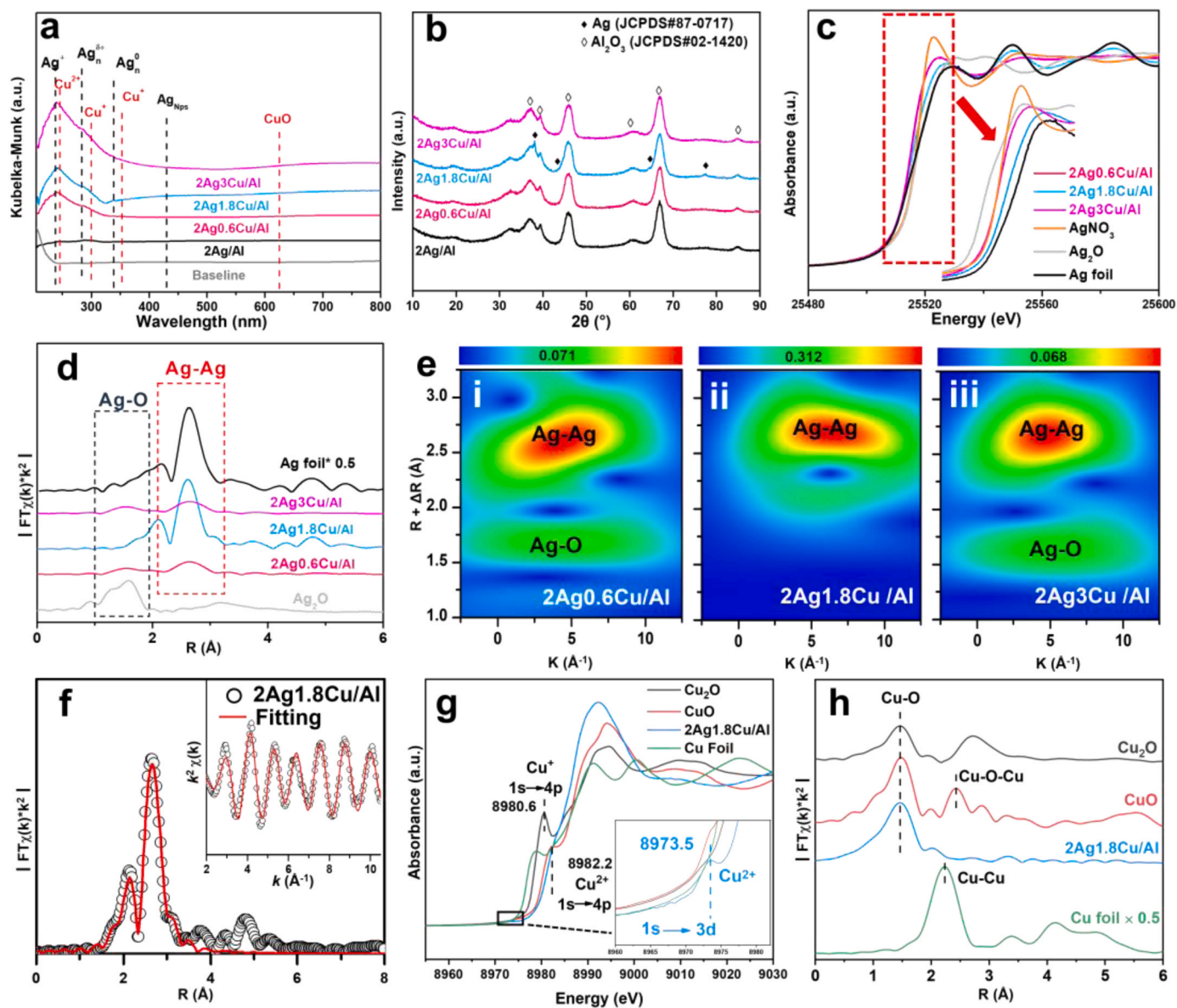


Fig. 3. Structure characterization of the 2AgxCu/Al samples: (a) UV-vis absorption spectra; (b) XRD patterns; (c) Ag K-edge XANES; (d) Ag K-edge EXAFS; and (e) WT of (i) 2Ag0.6Cu/Al, (ii) 2Ag1.8Cu/Al, and (iii) 2Ag3Cu/Al samples; (f) the 2Ag1.8Cu/Al EXAFS fitting curve in R- and k-(inset) spaces; (g) Cu K-edge XANES; (h) Cu K-edge EXAFS.

catalysts were between those of Ag foil and AgNO₃, indicating that the Ag species in the 2AgxCu/Al catalysts were in a mixed form of Ag⁰ and Ag⁺. The valence states of Ag species in 2Ag0.6Cu/Al and 2Ag3Cu/Al were similar because their white lines almost overlapped. However, the Ag species in the 2Ag1.8Cu/Al sample were much closer to Ag foil than those in 2Ag0.6Cu/Al and 2Ag3Cu/Al [59,60]. This indicates that more metallic Ag species existed in the 2Ag1.8Cu/Al sample, consistent with the X-ray photoelectron spectroscopy results (Supplementary Fig. S8). This conclusion was further confirmed by Fourier-transformed Ag-K EXAFS, as shown in Fig. 3d. The characteristic peak of the Ag-Ag metallic bond at 2.67 Å (phase uncorrected) was observed for the Ag foil as well as the 2Ag0.6Cu/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al samples [61]. In addition, the Ag-Ag coordination shell intensity for 2Ag1.8Cu/Al was much stronger than that for the 2Ag0.6Cu/Al and 2Ag3Cu/Al samples.

The wavelet transform (WT) analysis of the k²-weighted EXAFS signal was performed to distinguish the backscattering atoms in greater detail, and the WT contour plots are shown in Fig. 3e. Two WT intensity maxima were observed for the 2Ag0.6Cu/Al and 2Ag3Cu/Al samples,

with one at 1.5–2.0 Å due to the Ag-O coordination shell and the other at ca. 2.2–3.0 Å, which could be assigned to the Ag-Ag coordination shell (Fig. 3e–i,iii). In contrast, the 2Ag1.8Cu/Al sample only displayed one WT maximum at ca. 2.2–3.0 Å owing to the Ag-Ag coordination shell (Fig. 3h,ii).

The EXAFS curve fitting was conducted to acquire quantitative structural parameters of Ag in the 2Ag1.8Cu/Al catalyst, and the fitting parameters and curves are shown in Fig. 3f. The coordination numbers of Ag-Ag bonds were ca. 2.0, 7.1, and 2.0 in 2Ag0.6Cu/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al, respectively [62–64] (Supplementary Table S1 and Fig. S9). In addition, judging from the colormap intensity, the Ag-Ag bond intensity in the 2Ag1.8Cu/Al sample was considerably higher than those in 2Ag0.6Cu/Al and 2Ag3Cu/Al. These results indicate that there were more Ag nanoparticles within the 2Ag1.8Cu/Al catalyst, and the lower or higher Cu loading could make Ag species more dispersed [32, 65]. Fig. 3g presents the XANES patterns of the Cu K-edge for the 2Ag1.8Cu/Al catalyst and reference samples. The peak observed at 8982.2 eV indicated electron transfer between the 1 s and 3d orbitals of

the Cu^{2+} species, confirming the presence of Cu^{2+} species in the 2Ag1.8Cu/Al catalyst. In addition, the 8980.6 and 8982.2 eV peaks correspond to electron transfers from the 1 s to 4p orbitals of Cu^+ in Cu_2O and Cu^{2+} in CuO , respectively [66]. In the R-space EXAFS (Fig. 3h), a discernible peak was observed in the Cu-containing samples, attributed to the Cu–O coordination shell (ca. 1.4 Å, phase uncorrected). In addition, no evidence of Cu–Cu, Cu–Ag, or Cu–O–Cu scattering was detected in 2Ag0.6Cu/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al, respectively, providing further evidence that Cu predominantly existed as a highly dispersed Cu^{2+} and Cu^+ species.

Because the Cu introduction affects Ag dispersion, we further examined the influence of the Cu and Ag loading sequence on the Ag dispersion state. Catalysts represented as 1.8Cu/2Ag/Al and 2Ag/1.8Cu/Al were prepared by sequentially supporting Ag or Cu and then Cu or Ag, respectively. Although both catalysts did not show significant Ag characteristic peaks in the XRD patterns (Supplementary Fig. S10), significant peaks were observed in the STEM results for the 1.8Cu/2Ag/Al and 2Ag/1.8Cu/Al samples. The attached Ag particles have average particle sizes of 15.3 and 24.7 nm, respectively (Supplementary Fig. S10), while Cu remains highly dispersed on the Al_2O_3 surface. These results clearly show that Cu atoms could preferentially occupy the terminal hydroxyl groups regardless of the loading order. Thus, there were not enough anchoring sites on the $\gamma\text{-Al}_2\text{O}_3$ surface, leading to the aggregation of Ag atoms.

3.4. Oxygen activation capacity and $\text{NH}_3\text{-SCO}$ performance

Our previous studies have proven that the excellent O_2 activation ability of Ag_{NPs} with large particle sizes was the main reason for the superior $\text{NH}_3\text{-SCO}$ performance [29,32]. Therefore, we further compared the oxygen activation ability and the corresponding $\text{NH}_3\text{-SCO}$ performance between the samples with different Ag:Cu ratios.

In situ Raman spectroscopy was used to observe the state of oxygen species on the surface of different samples. As shown in Fig. 4a, under 10 vol% O_2/N_2 , the peaks at 245, 546, 670, 907, and 1038 cm^{-1} were attributed to adsorbed atomic oxygen (O), peroxy (O_2^-), molecular O_2 , O_2 with migrated electronic states, and superoxide (O_2^-), respectively [67–69]. To confirm that the Raman shifts for different oxygen species are located at the same positions as reported in literature, we pretreated the samples with N_2 or 10 vol% H_2/N_2 to exclude the influence of moisture and other impurities (Supplementary Fig. S11). The O_2 activation capacity of single-metal catalysts was tested using *in situ* Raman spectroscopy, and these catalysts were found to have poor O_2 activation ability (Supplementary Fig. S12). Compared to the single-metal catalysts, the 2AgxCu/Al serial catalysts exhibited excellent O_2 activation ability due to the addition of Cu, which induced the aggregation of Ag species. On the 2Ag0.6Cu/Al sample, as shown in Fig. 4a, the surface oxygen species were dominated by molecular oxygen, with a strong Raman shift observed at 670 cm^{-1} . The activated oxygen species, including O_2 with migrated electronic states at 907 cm^{-1} and O_2^- at

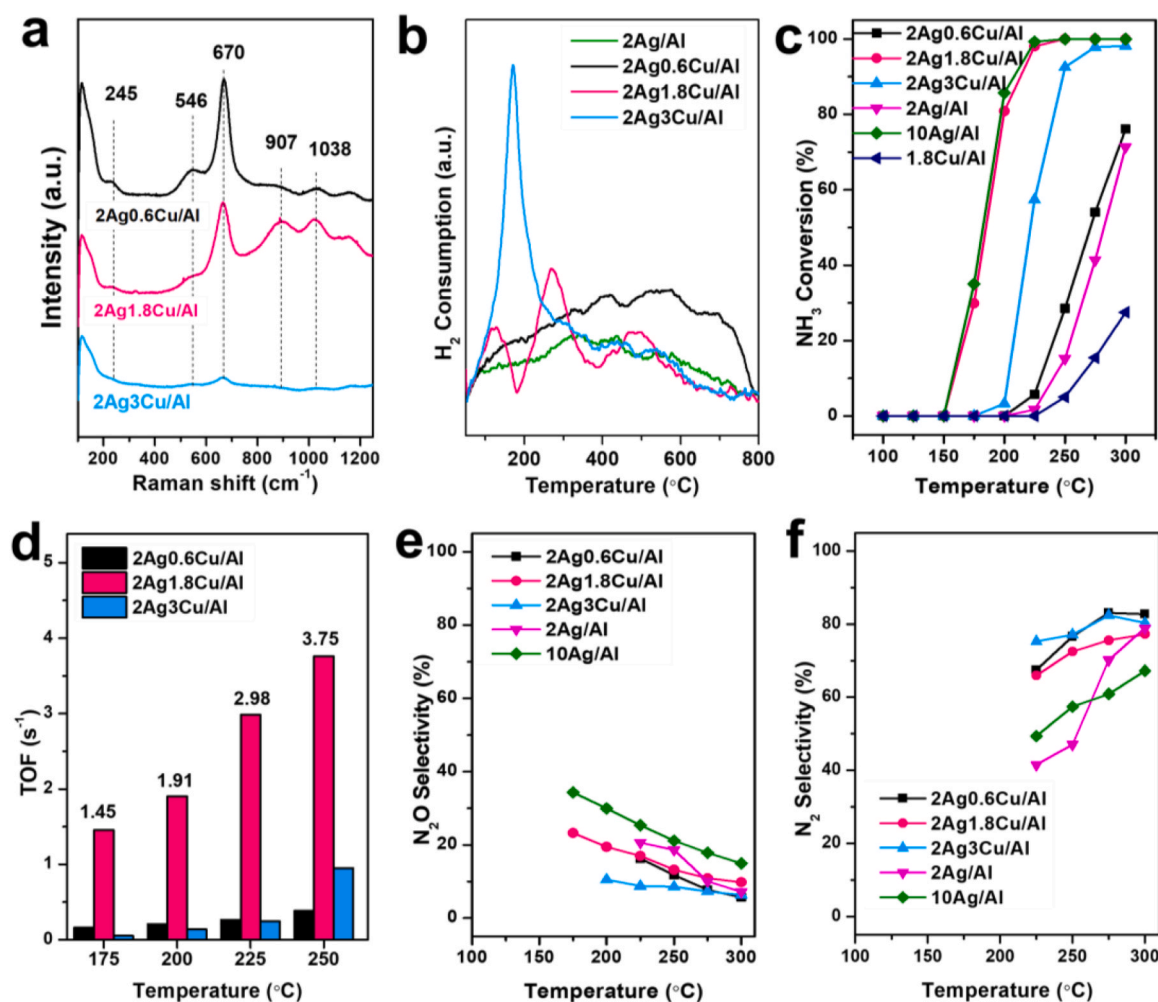


Fig. 4. *In situ* Raman spectra, H_2 -TPR profiles, $\text{NH}_3\text{-SCO}$ performance on 2Ag0.6Cu/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al catalysts: (a) *In situ* Raman spectra under 10 vol% O_2/N_2 at 175 $^{\circ}\text{C}$, (b) H_2 -TPR profiles, (c) $\text{NH}_3\text{-SCO}$ activity results, (d) calculated TOF of NH_3 conversion, (e) N_2O selectivity, and (f) N_2 selectivity. Reaction conditions: $\text{NH}_3 = 500$ ppm, $\text{O}_2 = 10$ vol%, and GHSV = 120,000 h^{-1} .

1038 cm^{-1} , were also present on 2Ag0.6Cu/Al. Obviously, the surface oxygen species on the 2Ag1.8Cu/Al sample were more abundant, and the proportion of activated oxygen species was significantly increased compared with that on 2Ag0.6Cu/Al. Moreover, the abundance of activated oxygen species on 2Ag1.8Cu/Al was greater than that of the other two oxygen species (O_2 with migrated electronic states and superoxide) at different temperatures (Supplementary Figs. S13 and S14). In contrast, except for the weak molecular oxygen species (670 cm^{-1}), almost no other surface oxygen species were observed on the 2Ag3Cu/Al sample. These results suggest that the 2Ag1.8Cu/Al catalyst exhibited a much higher oxygen activation capacity due to the presence of a larger proportion of metallic Ag_{NPs} , which is consistent with our previous findings [31,32].

Similar conclusions can be drawn from H_2 -TPR results. As shown in Fig. 4b, the 2Ag/Al and 2Ag0.6Cu/Al samples did not show obvious H_2 consumption peaks at temperatures below 300°C . The low-temperature H_2 consumption peak gradually became more pronounced in samples with higher Cu contents. Notably, the reduction temperature of the 2Ag1.8Cu/Al sample (123°C) was considerably lower than that of 2Ag3Cu/Al (175°C), indicating that 2Ag1.8Cu/Al had a higher redox performance in the low-temperature range.

Further, we tested the 2Ag0.6Cu/Al, 2Ag1.8Cu/Al, and 2Ag3Cu/Al samples for NH_3 -SCO reaction using 2Ag/Al, 10Ag/Al, and 1.8Cu/Al samples as references to investigate the effect of Cu addition on the catalytic activity. Fig. 4c–f show that the low-loading single-component Ag or Cu samples (2Ag/Al or 1.8Cu/Al) showed poor NH_3 -SCO activity, with NH_3 conversion below 20% at 250°C . The activity of the 2AgxCu/Al serial catalysts was considerably higher than that of the single-component catalyst, particularly when the Ag:Cu molar ratio was 2:3 (2Ag1.8Cu/Al). The activity of the 2Ag1.8Cu/Al sample was considerably improved with NH_3 conversion above 90% at 200°C , which was almost identical to that of 10Ag/Al. To maintain consistent activity, the 'pre-occupied-anchoring-site' strategy could considerably reduce the catalyst cost to ca. one-fifth of that of the pure Ag-based catalyst. The calculated TOF results further indicate that the TOF of NH_3 on the 2Ag1.8Cu/Al sample was ca. 10 and 5 times those on the 2Ag0.6Cu/Al and 2Ag3Cu/Al samples, respectively (at 250°C ; Fig. 4d). These results correlate well with the changing trend of metallic Ag_{NPs} content within the samples. Thus, Cu introduction led to the agglomeration of low-loading Ag (2 wt%) to form Ag_{NPs} , improving its oxygen activation ability and, thus, the NH_3 -SCO performance. In addition, compared to pure Ag-based catalysts, Cu introduction significantly reduced N_2O , NO, and NO_2 formation (Fig. 4e and Supplementary Fig. S15), thus improving the N_2 selectivity (Fig. 4f). This is also consistent with the results reported in the literature [26,70]. Introducing Cu will cause changes in the existence state of Ag species and thus affect the oxygen activation ability, which may be the main reason for affecting N_2 selectivity. The oxygen species on the 2Ag0.6Cu/Al surface were mainly adsorbed O_2 molecules (Fig. 4a), which can only overoxidize NH_3 into small amounts of NO and N_2O (Fig. S15). Therefore, it showed a relatively low NH_3 conversion and slightly better N_2 selectivity. However, a large amount of highly active O_2^- and electronically transferred O appeared on the 2Ag1.8Cu/Al surface, causing NH_3 to be overoxidized into N_2O , NO, and NO_2 . The presence of numerous N_2O molecule was the main reason for its low N_2 selectivity (Fig. S15). As the Cu loading increased, the Ag_{NPs} on the 2Ag3Cu/Al surface were redispersed again, which reduced the O_2 activation ability of Ag_{NPs} and amplified the catalytic effect of Cu species. However, because of the weak O_2 activation ability of Cu species, N_2O production was considerably reduced, increasing N_2 selectivity on 2Ag3Cu/Al (Fig. S15).

To further study the impact of introducing Cu species on catalyst stability, the 2Ag-700/Al samples were prepared for comparison with 2Ag1.8Cu/Al because the sizes of Ag_{NPs} in both samples were similar. Indeed, the NH_3 conversion on 2Ag-700/Al and 2Ag1.8Cu/Al was nearly identical at 100°C – 300°C (Supplementary Fig. S16a). However, the 2Ag1.8Cu/Al catalyst maintained 100% NH_3 conversion at 400°C for

more than 48 h, while 2Ag-700/Al achieved only 100% NH_3 conversion for 2 h and completely lost the NH_3 -SCO activity after 8 h (Supplementary Fig. S16b). This may be because the hydroxyl anchoring sites on the surface of the 2Ag-700/Al catalyst prepared by the H_2 reduction method still existed [29,71], and the Ag_{NPs} were redispersed during the NH_3 -SCO reaction, resulting in a rapid decrease in activity. However, most of the hydroxyl binding sites on 2Ag1.8Cu/Al were occupied by Cu, and there was a lack of abundant hydroxyl binding sites available to redisperse Ag during the NH_3 -SCO process. Hence, the 2Ag1.8Cu/Al sample consistently maintained excellent stability during the NH_3 -SCO reaction.

To assess the resistance of the catalysts to H_2O , CO_2 , and SO_2 , NH_3 -SCO reactions were conducted under dry/wet, CO_2 and SO_2 on/off conditions at 400°C (Supplementary Fig. S17). H_2O exerted a noticeable effect on NH_3 -SCO of 2Ag0.6Cu/Al, with NH_3 conversion rapidly decreasing from 100% to ca. 91% at 400°C within 10 min after H_2O addition. However, for 2Ag0.6Cu/Al, the NH_3 conversion gradually recovered to the initial level within 10 min of turning off the H_2O . In contrast, the 2Ag1.8Cu/Al and 2Ag3Cu/Al catalysts were less pronouncedly affected by H_2O incorporation into the reaction atmosphere. In previous studies, H_2O competed with NH_3 for adsorption, where larger Ag_{NPs} tended to adsorb NH_3 more readily and smaller Ag_{NPs} had a higher affinity for H_2O molecules [71]. Given that the surface of 2Ag0.6Cu/Al contained smaller Ag_{NPs} , the competitive adsorption effect of H_2O was more pronounced. However, the larger size of Ag_{NPs} on the 2Ag1.8Cu/Al surface reduced the impact of competitive H_2O adsorption. Although the size of Ag_{NPs} in the 2Ag3Cu/Al sample was smaller than that in 2Ag1.8Cu/Al, Cu also served as an active center for NH_3 adsorption and oxidation. Consequently, with increasing NH_3 adsorption sites, the competitive adsorption effect caused by H_2O was diminished. Therefore, the H_2O tolerance of 2Ag1.8Cu/Al and 2Ag3Cu/Al was better than that of 2Ag0.6Cu/Al.

It was also observed that 1000 ppm CO_2 had a remarkable impact on the NH_3 -SCO activity of the 10Ag/Al catalyst. The NH_3 conversion on 10Ag/Al rapidly decreased from 100% to less than 20% within 20 min of CO_2 introduction. Adding Cu to the catalyst component enhanced the CO_2 resistance to a certain extent. With higher Cu loading, the negative impact of CO_2 was less pronounced. For example, the 2Ag1.8Cu/Al and 2Ag3Cu/Al catalysts were almost unaffected by CO_2 , maintaining 100% NH_3 conversion at 400°C . This may be attributed to Cu acting as a sacrificial site and introducing Cu that alleviated the competitive CO_2 and NH_3 adsorption on Ag_{NPs} [72,73]. Furthermore, CO_2 conversion experiments were performed using 2Ag-400/Al, 2Ag-700/Al, and 2Ag-900/Al catalysts (Supplementary Fig. S18) to exclude the effect of size. The results showed that with the CO_2 introduction, the NH_3 conversion rate in all samples decreased rapidly, and the activity gradually returned to a certain level after CO_2 was removed. Therefore, the CO_2 tolerance of the catalyst was independent of the size of Ag_{NPs} [71].

Usually, Ag-based catalysts are very sensitive to SO_2 poisoning. However, in this study, the Ag– $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalysts exhibited high tolerance to SO_2 , and their sulfur resistance increased with increasing CuO_x loading. For instance, the 2Ag3Cu/Al sample was almost unaffected by SO_2 addition at 400°C , while the 10Ag/Al sample became completely inactive after 20 min of SO_2 introduction (Supplementary Fig. S17). SO_2 switching experiments were conducted on 2Ag-400/Al, 2Ag-700/Al, and 2Ag-900/Al to eliminate the influence of Ag_{NPs} size, and the results are presented in Fig. S18. These pure 2Ag-T/Al catalysts lost their NH_3 -SCO activity completely within 20 min of introducing SO_2 , and the activity did not recover after SO_2 was removed. SO_2 showed a substantial poisoning effect on pure Ag-based catalysts, independent of the Ag_{NPs} size [74]. In the Ag– $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalysts, the resistance to SO_2 increased with Cu loading. This could be attributed to the fact that Cu acted as SO_2 adsorption sites and sacrificial sites to a certain extent. Once the CuO_x was sulfated, it was easy to form CuSO_4 and continue to adsorb NH_3 . Moreover, the adsorbed NH_3 was not easy to desorb and activate and would subsequently react with sulfate to form $(\text{NH}_4)_2\text{SO}_4$

[75]. Therefore, increasing the Cu loading actually induced more sacrificial sites, considerably alleviating the SO_2 poisoning of the active centers of Ag_{NPs} , thereby enhancing the sulfur resistance of the catalyst.

Therefore, the co-existence of Ag and CuO_x species in the catalysts reported in this work improved the resistance to H_2O , CO_2 , and SO_2 to a certain extent, which was very beneficial for practical applications. Furthermore, the sequential impregnation of Ag and Cu significantly reduced the Ag_{NPs} agglomeration (Supplementary Fig. S10). This reduction in agglomeration played a pivotal role in causing the lower NH_3 -SCO observed on 1.8Cu/2Ag/Al and 2Ag/1.8Cu/Al compared with that on 1.8Cu2Ag/Al (Supplementary Fig. S19). NH_3 -TPD results suggested that the differences in the acidity of acid sites among 2Ag1.8Cu/Al, 1.8Cu/2Ag/Al, and 2Cu/1.8Ag/Al were insignificant (Supplementary Fig. S20).

However, the NH_3 -SCO activity of the catalyst did not increase linearly with the increase in the Ag_{NPs} size under limited Ag loading. The size of Ag_{NPs} usually affects the Ag oxidation state; e.g., larger Ag_{NPs} were associated with higher Ag metal content (as shown in Fig. 3c). The increase in the metal (Ag^0) content was conducive to improving the NH_3 -SCO activity. However, the number of active sites was considerably reduced when the nanoparticle size exceeded a certain threshold, resulting in a decrease in the apparent activity [71]. In addition, Cu species also exhibited certain NH_3 -SCO activity, which could be increased with elevated Cu loading [76]. Therefore, the excellent NH_3 -SCO performance of the 2Ag1.8Cu/Al catalyst was mainly attributed to the combined effects of increased Ag_{NPs} size, lowered Ag valence state, and Cu activity, all of which originated from the Cu 'pre-occupied-anchoring-site' effect.

In addition, we conducted a mechanistic study on 10Ag/Al and 2Ag1.8Cu/Al catalysts by *in situ* DRIFTS (Supplementary Section 10; Figs. S21–S29). The NH_3 adsorbed on the 10Ag/Al catalyst underwent profound dehydrogenation, forming N_2^- species. The oxidation of these N_2^- species resulted in substantial N_2O production, thereby establishing the primary influence of intermediate product N_2^- on the N_2 selectivity of the 10Ag/Al catalyst. However, introducing Cu atoms could inhibit the deep dehydrogenation of $-\text{NH}_x$ species to $-\text{N}$ species and thus limit the formation of N_2^- [31,77,78]. Although the $-\text{NH}_x$ species on the 2Ag1.8Cu/Al catalyst would also be oxidized to produce N_2O , the N_2O yield was significantly lower than that of 10Ag/Al. Therefore, the introduction of Cu atoms not only inhibited N_2^- formation on the

2Ag1.8Cu/Al catalyst but also facilitated the generation of intermediate products such as $-\text{N}_2\text{H}_4$ and $-\text{HNO}$, resulting in a substantial N_2 selectivity enhancement during NH_3 -SCO.

3.5. A universal mechanism of pre-occupied-anchoring-site strategy

We showed that Cu atoms could occupy the anchor sites of Ag to agglomerate Ag into Ag^0 nanoparticles. It was hypothesized that when other metals with greater anchoring strength to the hydroxyl group than Ag exist on Al_2O_3 , the co-loading of Ag with these metals might also lead to Ag agglomeration into large Ag_{NPs} on the Al_2O_3 surface. For this purpose, the anchoring strength of several transition metals to the hydroxyl groups on Al_2O_3 was calculated, and the results are displayed in Fig. 5. The energies of Co, Mn, Fe, and Ni anchoring to the terminal hydroxyl groups on Al_2O_3 were -8.34 , -9.49 , -8.69 , and -4.83 eV, respectively, all more negative than the anchoring energy of Ag (-4.78 eV). These results suggest that the transition metals considered could have a high potential to preoccupy the anchor sites of Ag. Experimentally, when Al_2O_3 was loaded with these metals, the concentrations of terminal and doubly bridging hydroxyl groups on the Al_2O_3 surface were greatly reduced (Supplementary Fig. S30).

The NH_3 -SCO activity test results revealed that the catalytic performance of AgMO_x/Al (M = other metals coloaded with Ag) was much higher than that of 2Ag/Al (Fig. 6a). The XRD patterns of 2Ag1.6Co/Al, 2Ag1.5Mn/Al, 2Ag1.6Fe/Al, and 2Ag1.6Ni/Al all showed characteristic peaks of Ag^0 (Fig. 6b). These results suggest that Co, Mn, Fe, and Ni preoccupied the anchor sites of Ag, leading to Ag agglomeration and resulting in enhanced NH_3 -SCO activity. The STEM results also confirmed this conclusion. For example, the average sizes of Ag_{NPs} in 2Ag1.6Co/Al, 2Ag1.5Mn/Al, 2Ag1.6Fe/Al, and 2Ag1.6Ni/Al were 26.6, 48.8, 11.9, and 25.8 nm, respectively, and only Ag was heavily agglomerated, whereas Co, Mn, Fe, and Ni were highly dispersed on the Al_2O_3 surface. In addition, the main byproduct during the NH_3 -SCO reaction in the AgMO_x/Al catalyst system was N_2O (Supplementary Figs. S31–S34 for product analysis), a characteristic byproduct of catalysts with Ag_{NPs} as active centers. Considering that 5.4Co/Al, 5.1Mn/Al, 5.2Fe/Al, and 5.4Ni/Al showed relatively low NH_3 -SCO activity, the main active centers of AgMO_x/Al catalysts were still Ag_{NPs} . This suggests that Co, Mn, Fe, and Ni also showed a 'pre-occupied-anchoring-site' effect. Notably, the various metals used as placeholders showed different

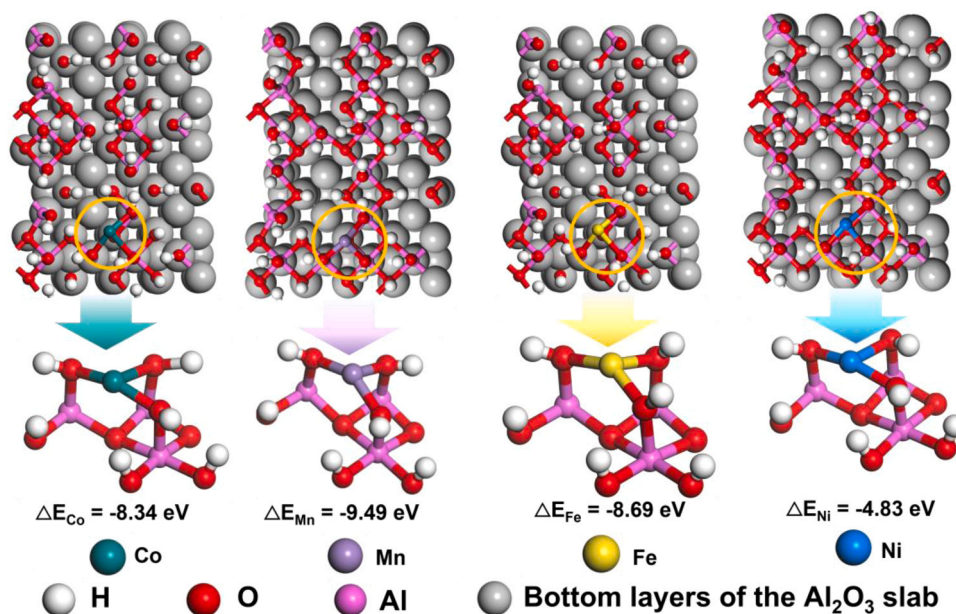


Fig. 5. DFT calculation results for the anchoring capability of Co, Mn, Fe, or Ni on the $\gamma\text{-Al}_2\text{O}_3$ (100) surface.

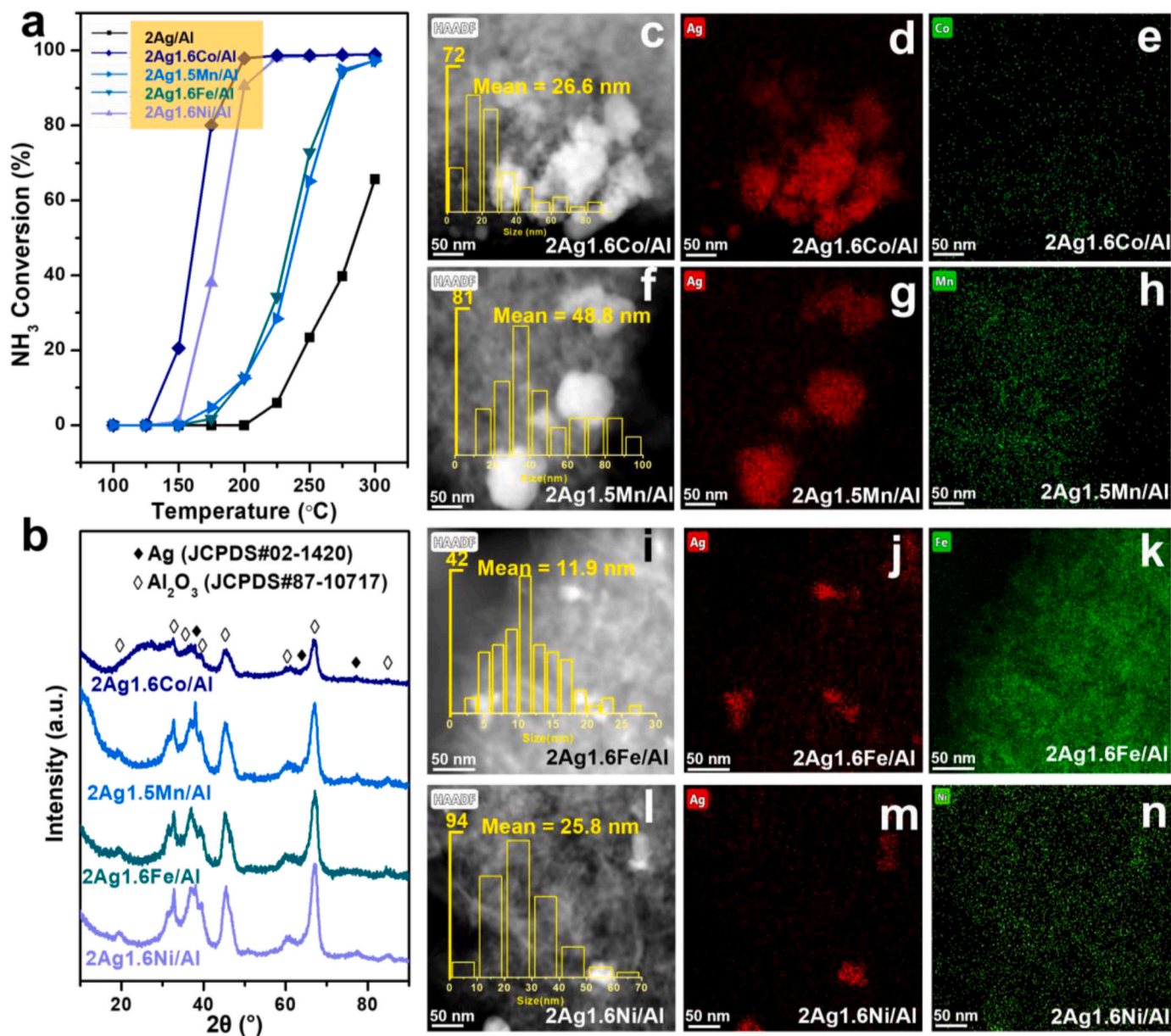


Fig. 6. NH_3 -SCO performance tests and structural properties of 2Ag1.6Co/Al, 2Ag1.5Mn/Al, 2Ag1.6Fe/Al, and 2Ag1.6Ni/Al catalysts: (a) NH_3 -SCO test; (b) XRD patterns; HAADF-STEM images and EDS mapping of (c–e) 2Ag1.6Co/Al, (f–h) 2Ag1.5Mn/Al, (i–k) 2Ag1.6Fe/Al, (l–n) 2Ag1.6Ni/Al.

anchoring strengths on the hydroxyl groups on the Al_2O_3 surface, which could affect the dispersion of Ag species to a certain extent, resulting in different NH_3 -SCO activities and N_2 selectivity.

4. Conclusion

Based on the observation that Cu preferentially anchors on the surface hydroxyl groups of $\gamma\text{-Al}_2\text{O}_3$ over Ag, we propose a ‘pre-occupied-anchoring-site’ strategy to construct more efficient NH_3 -SCO active sites. This strategy employed cheaper Cu to preferentially occupy the anchoring sites, inducing the aggregation of Ag. The low-loading Ag species were successfully agglomerated into highly dispersed Ag_{NPs} using a simple wet impregnation method. This approach reduced the catalyst cost to *ca.* one-fifth while ensuring consistent catalytic activity. When the Ag loading was 2 wt% and the Ag:Cu molar ratio was controlled at 2:3 (2Ag1.8Cu/Al), Ag atoms agglomerated into Ag_{NPs} on the $\gamma\text{-Al}_2\text{O}_3$ surface due to the limited availability of anchoring sites, thus exhibiting excellent NH_3 -SCO activity similar to that of 10 wt% Ag/

Al_2O_3 catalyst. The synergistic effect between the Cu and Ag components contributed to improved N_2 selectivity, H_2O , SO_2 resistance, and catalytic stability. This ‘pre-occupied-anchoring-site’ strategy has broad applicability to various inexpensive transition metals, such as Mn, Co, Ni, and Fe. These metals can pre-occupy the Ag anchoring sites, forcing the more expensive Ag to agglomerate into Ag_{NPs} . This cost-effective ‘pre-occupied-anchoring-site’ mechanism offers a promising avenue for designing cheaper, more efficient, and stable nanoparticle materials for heterogeneous catalysis applications.

CRediT authorship contribution statement

F. W. conceived and supervised the project. Z. L. performed the experiments, DFT calculations and wrote the manuscript. S. X. assisted with the experiments. C. Z., P. N. and H. H. assisted with the interpretation of experimental results. F. L., K. L. and X. C. Z. directed the study and assisted with manuscript writing. All authors discussed the results and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123655](https://doi.org/10.1016/j.apcatb.2023.123655).

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